

PATENT SPECIFICATION

NO DRAWINGS

Inventors: FERDINAND BODESHEIM, GERHARD DIETER WOLF, ULRICH
BAHR and GUNTHER NISCHK

1.194.607



1.194.607

Date of Application and filing Complete Specification: 8 April, 1968.

No. 16695/68.

Application made in Germany (No. F52571 IVd/39c) on 1 June, 1967.

Complete Specification Published: 10 June, 1970.

Index at acceptance: —C3 R(22D1A2, 22D1AX, 22D1B2, 22D1BX, 22D2A2, 22D2AX, 22D2BX, 22D3B, 22D3C, 22D3D1, 22D3DX, 22N1B); C2 C(2D43D, 2D43E, 2D43S2, 2D43Z2)

International Classification: —C 08 g 20/02

COMPLETE SPECIFICATION

High Molecular Weight Polyamides Containing Disulphimide Groups

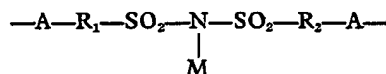
We, FARBENFABRIKEN BAYER AKTIEN-
GESELLSCHAFT, a body corporate, organised
under the laws of Germany, of 509, Lever-
kusen, Germany, do hereby declare the in-
vention, for which we pray that a patent may
be granted to us, and the method by which
it is to be performed, to be particularly
described in and by the following state-
ment:—

10 This invention relates to co-polyamides
containing disulphimide groups and to a pro-
cess for their preparation.

15 The macromolecular co-polyamides which
are obtained by melt condensation of di-
ammonium salts of dicarboxylic acids or poly-
merisation of lactams usually cannot be dyed
with basic dyes.

20 In order to be able to use the wide
range of basic dyes available for dyeing co-
polyamides, it was necessary to impart to the
polyamide the necessary affinity for these
dyes by introducing acid groups. It was known
that the number of acid groups at the ends
of the polymer chains can be increased by
25 using dicarboxylic acids as chain terminating
agents. Owing to the shortening in the average
chain length of the polyamide which results,
this process is only of very limited value. It
is also known that the uptake of dyes by co-
polyamides can be improved by the addi-
30 tion of co-condensable sulphonc acid deriva-
tives. These compounds include, for example,
aliphatic or aromatic diaminosulphonic acids,
or aminocarboxylic acids which contain sul-
35 phonic acid groups.

According to this invention there are pro-
vided a high molecular weight co-polyamide
containing structural segments of the formula



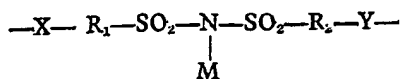
wherein R₁ and R₂ each represent an aromatic 40
radical, A represents an amide group of the
formula —NH—CO— or —CO—NH— and
M represents a hydrogen atom or an alkali
metal atom, said polyamide having a relative
solution viscosity η_{rel} (measured at a solu- 45
tion of 1g of polymer in 100 ml m-cresol
at 20°C) of above 2.0.

Also according to this invention there is
provided a process for the production of such
high molecular weight co-polyamides, which 50
comprises polycondensing aromatic disulph-
imides which contain primary amino and/or
carboxylic acid groups with polyamide-
forming compounds, said polycondensing
being effected in the melt at temperatures 55
between 150 and 300°C.

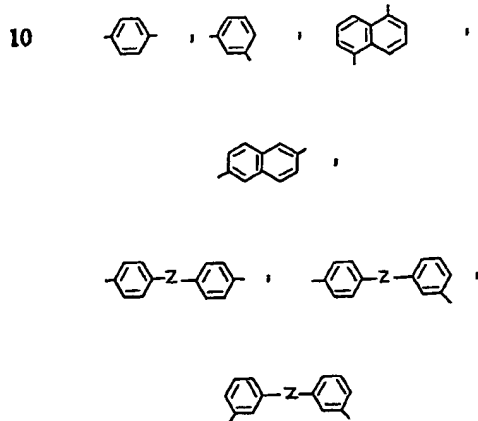
The co-polyamides of the invention can
readily be dyed with basic dyes.

If the disulphimide contains two amino 60
groups, a dicarboxylic acid such as adipic
acid, suberic acid, sebacic acid or tere-
phthalic acid is added to the polycondensation
reaction mixture in order to achieve high
molecular weights, whereas if the disulphimide
contains two carboxylic acid groups it is 65
necessary to add a diamine such as hexa-
methylenediamine or octamethylenediamine.
In each case the compounds are used pre-
ferably in equivalent quantities based on the
NH₂ or COOR groups of the disulphimide. 70

The aromatic disulphimides correspond to
the general formula



- wherein X and Y, which may be different or not, represent an NH₂ group or a COOR group (R represents a hydrogen atom or a lower that is C₁—C₄ alkyl radical); M represents a hydrogen atom or an alkali metal atom; R₁ and R₂, which may be different or not, each represent an aromatic radical, for example one of the following formulae:



- (Z=alkylene, CO—, —O—, —S—, or —SO₂).

- The following compounds are examples of suitable disulphimides which correspond to the formula given above: 4,4' - Diamino-diphenyl - disulphimide; 4 - amino - 4' - carboxy - diphenyl - disulphimide; diphenyl-disulphimide - dicarboxylic acid - (4,4'); 3, 4' - diamino - diphenyl - disulphimide; 3,3' - diamino - diphenyl - disulphimide; dimethyl ester of diphenyl - disulphimide - 3,3' - dicarboxylic acid; 3 - amino - 4' - carboxy - diphenyl - disulphimide; 4 - amino - 3' - carboxy - diphenyl - disulphimide; diphenyl-disulphimide - 3,4' - dicarboxylic acid; 3 - amino - 3' - carboxy - diphenyl - disulphimide; 4 - (p - amino - phenoxy) - 3' - amino - diphenyl - disulphimide and 5 - amino - 4' - amino - naphthyl(1) - phenyl-disulphimide.

- It is surprising that the above mentioned diaryl-disulphimides can be co-condensed directly with normal polyamide-forming compounds at the required temperatures of 250°C or more since sulphonic acid amides usually are not stable under these conditions. The addition of sulphonamides to polyamide melt usually results in polymers which become discoloured relatively quickly.

- The diaryl-disulphimides can be prepared by reacting sulphonic acid chlorides with sulphonic acid amides in an alkaline medium.

The disulphimide-containing co-poly-

amides which can be dyed with basic dyes are advantageously prepared by adding the disulphimides to the polyamide-forming monomers before condensation begins, if desired, with the addition of dicarboxylic acids or diamines, and then carrying out the thermal condensation of polymerisation reaction in known manner in an inert atmosphere.

The addition of disulphimides may be varied within wide limits so that polymers containing 15 mMol to 600 mMol of the disulphimide groups per kg of polymer material are obtained. The amount of disulphimide used is preferably so chosen that the polymer contains 50 to 250 mMol per kg.

The diphenyldisulphimides may be used as co-monomers in the production of any copolyamides. The co-polyamides can be prepared from lactams such as caprolactam or dodecanolactam or from the salts of dicarboxylic acids such as adipic acid, suberic acid, or sebacic acid with diamines such as hexamethylene diamine, octamethylene diamine or decamethylene diamine or from aminocarboxylic acids such as ε-aminocaproic acid or ω-aminoundecanoic acid, by condensation in the melt.

The co-polyamides prepared according to the invention are colourless and can be dyed very satisfactorily with basic dyes. They can easily be worked up by known processes into shaped articles, filaments, fibres or bristles. The dyed textiles are particularly fast to washing.

The following examples are to further illustrate the invention.

EXAMPLE 1

- a) Sodium bis - (m - aminophenyl) - disulphimide

190 Parts by weight of a 21% by weight aqueous sodium hydroxide solution are added to a suspension of 202 parts by weight of m-nitro-benzene sulphonamide in 1200 parts by weight of water. 243 Parts by weight of m-nitrobenzene sulphochloride dissolved in 400 parts by weight of acetone and 244 parts by weight of an 18% by weight aqueous sodium hydroxide solution are now added dropwise at room temperature at such a rate that the pH is maintained at 8 to 9. When the reaction mixture has subsequently been stirred for another 2 hours at 50°C, it is cooled, filtered by suction and washed with sodium hydroxide solution. The residue consists of di-(m-nitrophenyl)-disulphimide sodium (melting point 254 to 255°C) from which the diamino compound of m.p. 285 to 287°C is obtained by reduction.

- b) 85 Parts by weight of caprolactam, 10 parts by weight of ε-aminocaproic acid, 3.5 parts by weight of the disulphimide sodium prepared according to a) and 1.5 parts by

weight of adipic acid were condensed in an autoclave for 6 hours under an atmosphere of nitrogen. A colourless co-polyamide which had a relative solution viscosity of 2.75 (1% solution in m-cresol) and a melting point of 213 to 215°C was formed. The material could be spun into threads in known manner and the textiles produced from them could be dyed with basic dyes.

10

EXAMPLE 2

7 Parts by weight of di-(m-aminophenyl)-disulphimide sodium (see Example 1a) together with 3 parts by weight of adipic acid are mixed with 145 parts by weight of the salt of adipic acid and hexamethylene diamine and the mixture is then precondensed, first for 2 hours at 230°C in a closed apparatus, and then under nitrogen at 290°C for a further 6 hours. The resulting co-polyamide melted at 258 to 262°C and had a relative solution viscosity of 2.83 (1% solution in m-cresol). After it had been worked up into knitted textile pieces, the colourless polymer could be dyed very satisfactorily with basic dyes.

25

EXAMPLE 3

a) Bis - (m - methoxycarbonylphenyl) - disulphimide

A solution of 132 parts by weight of benzoic acid-3-sulphochloride in 150 parts by weight of dioxane and 210 parts by weight of a 28.6% sodium hydroxide solution are simultaneously added dropwise at 5 to 10°C to a solution of 120 parts by weight of benzoic acid-3-sulphonamide and 48 parts by weight of caustic soda in 450 parts by weight of water. The reaction mixture is stirred at room temperature for 2 hours and the disulphimide is then obtained by acidification with concentrated hydrochloric acid. The disulphimide is suspended in 5 times its own weight of methanol and is boiled under reflux for one hour while hydrogen chloride gas is passed through. The precipitate is filtered hot from sodium chloride. The disulphimide diester crystallises on cooling with 1 mol of methanol; m.p. 170°C.

b) 4 Parts by weight of the di-(m-methoxycarbonylphenyl)-disulphimide described under a) and 1.1 parts by weight of hexamethylenediamine were combined with 85 parts by weight of caprolactam and 10 parts by weight of ε-aminocaproic acid and condensed under nitrogen for 7.5 hours at 265°C. The co-polyamide obtained melted at 212 to 215°C and had a relative solution viscosity of 2.65 (1% solution in m-cresol). After extraction with water, the colourless granulate could be dyed with basic dyes.

60

EXAMPLE 4

a) Bis - (6 - carboxyphenyl) - disulphimide
A solution of 381 parts by weight of p-

toluenesulphochloride in 500 parts by weight of acetone and 300 parts by weight of 26.6% by weight aqueous sodium hydroxide solution are simultaneously added dropwise at 50°C to a solution of 342 parts by weight of p-toluenesulphonamide and 80 parts by weight of caustic soda in 1000 parts by weight of water at such a rate that the pH is maintained at 9 to 10. The reaction mixture is then stirred for a further 3 hours at 50°C, and sodium bis-(p-tolyl)-disulphimide (m.p. 323 to 326°C) is filtered off under suction after cooling.

65

70

75

145 Parts by weight of sodium bis-(p-tolyl)-disulphimide are added to a mixture of 105 parts by weight of caustic soda and 316 parts by weight of potassium permanganate in 4000 parts by weight of water and is boiled under reflux for 8 hours. The manganese dioxide is then removed by filtration under suction and bis-(p-carboxyphenyl)-disulphimide (m.p. 328 to 330°C) is obtained by acidification with concentrated hydrochloric acid. Bis-(p-carboxyphenyl)disulphide is obtained as the monosodium salt by treatment with the equivalent quantity of caustic soda in concentrated aqueous solution.

80

85

b) 4 Parts by weight of the monosodium salt of bis-(p-carboxyphenyl)-disulphimide were condensed with 1.1 parts by weight of hexamethylenediamine, 85 parts by weight of caprolactam and 10 parts by weight of ε-aminocaproic acid exactly as in Example 3b). A co-polymer which melted at 214 to 216°C and had a relative viscosity of 2.48 (1% solution in m-cresol) was obtained. No difference could be found between this product and the polymer described under 3b) in respect of the dyeability.

90

95

100

EXAMPLE 5

7.6 Parts by weight of the monosodium salt of 4-amino-3'-carboxy-diphenyl-disulphimide (obtainable in a manner analogous to Example 3a) from benzoic acid-3-sulphonamide and 4-nitrobenzenesulphochloride (m.p. above 340°C) were condensed with 10 parts by weight of ε-aminocaproic acid and 82.4 parts by weight of caprolactam for 5.5 hours at 270°C under an atmosphere of nitrogen. A co-polyamide of melting point 209 to 213°C and a relative viscosity 2.72 was obtained. Pieces of knitted fabric produced from the polymer after spinning could be dyed very satisfactorily with basic dyes, the dyes being fast to washing.

105

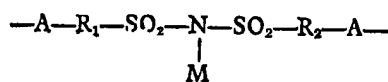
110

115

WHAT WE CLAIM IS:—

1. A high molecular weight co-polyamide containing structural segments of the formula

120



- wherein R_1 and R_2 each represent an aromatic radical, A represents an amide group of the formula $-\text{NH}-\text{CO}-$ or $-\text{CO}-\text{NH}-$ and M represents a hydrogen atom or an alkali metal atom, said polyamide having a relative solution viscosity η_{rel} (measured at a solution of 1 g of polymer in 100 ml m-cresol at 20°C) of above 2.0.
2. The high molecular weight co-polyamide of claim 1, said structural segments being present in such an amount, that said polyamide contains 15 to 600 mMol disulphimide groups per kg polymer.
3. A process for the production of high molecular weight co-polyamides according to claim 1, which comprises polycondensing aromatic disulphimides which contain primary amino and/or carboxylic acid groups with polyamide-forming compounds, said polycondensing being effected in the melt at temperatures between 150 and 300°C.
4. The process of claim 3, an equivalent quantity to said aromatic disulphimide of diamine or dicarboxylic acid being added.
5. A process for the production of high molecular weight co-polyamides substantially as herein described with reference to the Examples.
6. High molecular weight co-polyamides when prepared by the process claimed in any one of claims 3 and 5.
- ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54, High Holborn,
London, W.C.1.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.